

## **Standard Operating Procedure for the Toxicity Characteristic Leaching Procedure (TCLP) Extraction for the Determination of Volatile Organic Compounds**

### **1.0 Scope and Application**

This Standard Operating Procedure (SOP) will describe the procedure to be used when performing the TCLP extraction for the determination of volatile organic compounds in solid, liquid, and multiphasic matrices. The extraction procedure is based on Method 1311 from SW846. Extracts obtained by this procedure are analyzed by SOP I-2-35, the Standard Operating Procedure for the Analysis of Purgeable Organic Compounds (VOC's) in water by Capillary Column Gas Chromatography/Mass Spectrometry. Analytes that can be measured using this procedure are listed below alphabetically along with the analyte number assigned to that compound in the Chemistry Division's Laboratory Information Management System(LIMS).

<u>Analyte</u>	<u>Analyte Number</u>
Acetone	40582
Benzene	40502
2-Butanone	40592
Carbon tetrachloride	40522
Chlorobenzene	40752
Chloroform	40702
1,4-Dichlorobenzene	40572
1,2-Dichloroethane	40532
1,1-Dichloroethylene	40552
Hexachlorobutadiene	41137
Tetrachlorethene	40822
Trichlorethene	40542
Vinyl chloride	40512

All other analytes listed in SOP-I-2-35 are detectable by this procedure but are not TCLP analytes and thus are not required to be analyzed.

### **2.0 Summary of Method**

Solid, liquid, and mixtures are extracted under prescribed conditions. The sample must first be determined to be a solid, liquid, or a mixture. If the sample is 100% solid, it is extracted with TCLP fluid and the resulting liquid is defined as the TCLP extract. If the sample is a liquid(containing less than 0.5% dry solid material), then the liquid itself is defined as the TCLP extract. If the sample is a solid/liquid mixture, then the percent

solids must be determined by following the procedure described in SOP I-1-15, Section 8.1. The liquid portion of the sample is separated from the solid portion of the sample and then the solid is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. If solid material is present, it is extracted by weighing a portion of the sample into a special extraction vessel called a Zero-Headspace Extractor (ZHE), adding the appropriate amount of extraction fluid, closing and pressurizing the ZHE, and rotating the ZHE for  $18 \pm 2$  hours. After the rotation is complete, the liquid from the ZHE is extruded under pressure into special sample bags. This liquid is defined as the TCLP extract. For quality assurance/quality control, spikes are added post extraction at the time of analysis. A portion of the extract is then analyzed by SOP I-2-35.

### **3.0 Definitions**

Lab blank - A TCLP extraction performed with no sample in the extraction vessel for the purpose of determining background levels of volatiles. A soil blank is not typically done because the soils usually analyzed are unique in character and a soil blank is not meaningful.

### **4.0 Interferences**

Contaminant sources are unavoidable when performing this procedure. Analysis of laboratory blanks provides information about the presence of contaminants. Some atmospheric exposure of the sample and extract is required when doing this procedure. This exposure time must be kept to a minimum. Because of this atmospheric exposure, the subtraction of blank values from sample results is permitted.

### **5.0 Safety**

- 5.1 The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined, therefore each chemical should be treated as a potential health hazard and exposure to these chemicals should be minimized.
- 5.2 This method does not address all safety issues associated with its use. This laboratory is responsible for maintaining a safe work environment and a current awareness of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets(MSDS's) should be available to all personnel involved in this analysis.

### **6.0 Supplies and Equipment**

- 6.1 Zero Headspace Extractors(ZHE's) - The ZHE must be assembled during use and consists of several parts including but not limited to a base plate, cylinder, top

plate, piston, O-rings, screens, and filters. ZHE's are available from several commercial sources. As of this revision of this SOP, ZHE's from Millipore are in use. They can be purchased through Fisher and the part number for a complete extraction vessel is YT30-090-HW.

- 6.2 pH meter
- 6.3 Nitrogen gas supply at low pressure - Nitrogen gas is used to set the pistons and to pressurize the ZHE's.
- 6.4 Glass fiber filters - TCLP glass fiber filters for use in the ZHE's during the extraction. Available from Gelman, product number 66256.
- 6.4 Syringes for adding TCLP fluid to the ZHE's. Large volume syringes are best because typically 500 mL fluid is added.
- 6.5 Sample rotation device.
- 6.6 Tedlar bags - These are bags made of inactive material for extract collection. These are available from Fisher and the catalog number is 09-735-44

## **7.0 Reagents and Fortified Solutions**

### **7.1 Reagents**

- 7.1.1 Certified buffer solutions at pH's of 4, 7, and 10 for the calibration of the pH meter.
- 7.1.2 Glacial acetic acid, ACS reagent grade
- 7.1.3 Sodium hydroxide, 1N made from ACS reagent grade
- 7.1.4 Reagent water - Laboratory distilled water purified by a Barnstead II water purification system. This system is a series of 4 cartridges designed to remove ions and organic compounds from the water.

### **Extraction**

#### **7.1.5 TCLP extraction fluid 1 - Commercially prepared TCLP**

Fluid 1 is available from Fisher. The catalog number is ST100-20. Alternatively, the extraction fluid may be prepared in the laboratory by using the procedure described in section 7.1.5.1. The use of commercially

prepared TCLP fluid is preferred as it generally yields cleaner extractions.

7.1.5.1 Preparation of TCLP extraction fluid 1 - Add 5.7 mL glacial acetic acid to 500 mL reagent water, add 64.3 mL of 1N sodium hydroxide and dilute to a volume of 1 liter. When correctly prepared, the pH of this fluid will be  $4.93 \pm 0.05$ .

Note: the extraction fluid should be monitored frequently for impurities. The pH should be checked prior to use to ensure that the fluid is made up accurately. If impurities are found or the pH is not within specifications, the fluid should be discarded and fresh extraction fluid prepared.

7.1.6 LFB Stock solution - EPA 524.2 VOC mix purchased from Supelco (Catalog number 4-7932). This solution contains all method analytes plus the remainder of the analytes that are tested for in SOP I-2-35 at 200 ug/mL. This stock solution must be a different stock solution than that which is used to prepare the calibration standards in SOP I-2-35.

7.2 Fortified solution preparation - Matrix and lab blank fortified solutions(spikes) are prepared post-extraction in this procedure. Some samples are too dirty and are prone to foaming so they must be diluted before undergoing purge and trap analysis. This must be determined on an individual sample basis. Typically samples are diluted 20 mL/200 mL. Whatever the individual situation, 200 mL volumes must be spiked. The spiked solution preparation is described in Section 7.2.1.

7.2.1 Dilute the LFB stock solution as indicated below. A 10 uL gas-tight syringe is required. Rinse the syringe five times with methanol. Then, using the syringe, puncture the cap on the vial of stock solution and rinse and discard 5 uL of stock 2 times. Then rinse the syringe in the stock solution several times to remove any trapped bubbles. When bubbles are no longer present, withdraw the indicated amount of stock and inject it into the 200mL volume to be fortified. Mix the contents by inverting the flask 3 times only. Excessive mixing may result in loss of analytes. Immediately transfer the spiked solution to labelled, prepared VOC vials. Cap and store the vials until ready for analysis.

$$\begin{aligned}\text{Spike solution} &= 2.5 \text{ uL}/200\text{mL} \\ &200 \text{ ug/mL} \times 0.0025\text{mL}/0.2\text{L} = 2.5 \text{ ug/L}\end{aligned}$$

## 8.0 Sample Collection, Shipping, and Storage

- 8.1 Samples are collected in screw-top air-tight containers that are sufficient in size to allow for multiple analyses. One hundred grams is usually the minimum amount of sample required for a sample that appears to be 100% solid. If the sample is a liquid or a liquid/solid mix then more sample is required. Samples are typically collected in half liter or liter jars and regardless of size, it is best to fill the container as full as possible.
- 8.2 Samples are not required to be shipped under special conditions. However, keeping the samples cool is beneficial when sampling volatiles. The sample must be stored at 4 degrees or lower once it reaches the laboratory.

## **9.0 Quality Control**

- 9.1 Minimum quality control requirements are the extraction of a one blank per extraction set. Currently, because we only possess 5 ZHE's, a sample set consists of 5 extractions. There are exceptions.
  - 9.1.1 In some cases several samples may need extraction. To expedite the extractions a blank may be done one time per week which would be one blank in 20 extractions.
  - 9.1.2 Three additional ZHE's are available but are a different design than the 5 mentioned in Section 9.1.1. These 3 are more difficult to use and require some minor changes in hardware when doing the extractions. It is recommended to not use these unless absolutely necessary.
- 9.2 A sample duplicate is recommended but not required. The analyst must determine if doing a duplicate will add significant time to the extraction and decide if a duplicate extraction is merited.
- 9.3 Blank and matrix spikes
  - 9.3.1 A blank spike must be prepared for each extraction set. The spike is prepared post-extraction as described in Section 7.2.1. The blank spike is prepared using the same extract as the blank as there should be about 500 mL volume. A second blank extraction for spiking is not required.
  - 9.3.2 The matrix spike is prepared from any one of the sample extracts. The spike is prepared post-extraction as described in Section 7.2.1. The matrix spike is prepared using the same extract as the selected sample as there should be about 500 mL volume. A second sample extraction for matrix

spiking is not necessary.

9.3.3 Correcting sample results for levels of analytes found in the blank is acceptable.

9.3.4 Correcting for sample levels when determining matrix spike recoveries is required.

9.4 TCLP extraction and analysis hold times

9.4.1 The TCLP volatiles extraction must be completed within 14 days of sample collection. The purge and trap analysis of these extracts must be completed within 14 days of the TCLP extraction.

9.4.2 If sample holding times are exceeded, the values obtained will be considered minimal concentrations. Exceeding the holding time is not acceptable in establishing that a waste does not exceed the regulatory level. Exceeding the holding time will not invalidate characterization if the waste exceeds the regulatory level.

9.5 Additional quality control requirements exist for the analysis of the extracts. They can be found in SOP I-2-35, Section 9.

**10.0 Calibration and Standardization**

This section is not applicable to this SOP

**11.0 Procedure**

11.1 Verify that the pH of the extraction fluid is  $4.93 \pm 0.05$ . The procedure for calibrating the pH meter will not be described here.

11.2 The TCLP extraction procedure will vary depending on if the sample is a solid, liquid, or a mixture. The procedure for each will be described separately. The addition of the extraction fluid is identical for each of the matrices and will be described in Section 11.2.4.

11.2.1 Solid sample TCLP extraction - Most samples are considered 100% solid and this procedure is the most routinely used.

11.2.1.1 Assemble the ZHE's to the point where the solid sample can be added.

- 11.2.1.1.1 Install the o-rings on the piston. There are several different sizes of o-rings so be sure to have the correct rings. Each piston requires 3 o-rings. Inspect the o-rings for flaws before installation. The wide end of the piston is the top and two identical o-rings go in the top grooves. The open-sided ring goes on the bottom with the open side facing the bottom of the piston.
- 11.2.1.1.2 Install the piston into the piston cylinder. The cylinders are directional - they have a distinct top and bottom. Adjust the cylinder so the bottom is facing up. Place the piston at the opening of the cylinder. Wet the o-ring on the piston with TCLP extraction fluid. Cover the piston with a paper towel to avoid splashing. Using the Teflon rods, pound the piston into the cylinder. This can take some effort. Once the piston is in the cylinder invert the cylinder and continue pushing the piston from the bottom until it is about 2 inches from the top of the cylinder.
- 11.2.1.1.3 Install the appropriate o-ring into the base plate of the ZHE. Inspect the o-ring for flaws.
- 11.2.1.1.4 Place the cylinder with the piston in it on the o-ring on the base plate. Be sure that is is level.
- 11.2.1.1.5 Install the appropriate o-ring into the top plate of the ZHE. Inspect the o-ring for flaws.
- 11.2.1.1.6 Install, in order, a mesh screen, two glass fiber filters, and a second mesh screen into the top plate of the ZHE.
- 11.2.1.1.7 Place the remaining o-ring on top of the mesh screen to hold it in place.

11.2.1.2 Add the sample to the ZHE

- 11.2.1.2.1 The sample should be kept cool until ready to weigh to minimize loss of volatile analytes.
- 11.2.1.2.2 Open the sample container and homogenize the sample as best as possible. In some cases, it is not possible at all.
- 11.2.1.2.3 Using a weigh boat, weigh by difference, about 25 grams of the solid into the top of the ZHE.
- 11.2.1.2.4 Install the top plate onto the ZHE immediately and tighten down with the 3 screws. Tighten the screws evenly - do not tighten one all the way and then move on to the next. Be sure that the valve is closed to minimize volatile losses.

11.2.1.3 Set the piston inside the ZHE - The piston must be set as high as possible inside the ZHE to minimize headspace using the house nitrogen gas supply.

- 11.2.1.3.1 Set the nitrogen flow before making the connection to the ZHE. The flow should be minimal to reduce the chances of rupturing the filters inside the ZHE.
- 11.2.1.3.2 Connect the ZHE to the nitrogen supply using Swagelok connectors. Make the connection at the Swagelok fitting on the bottom of the ZHE. Be sure the pressure relief valve on the bottom is closed.
- 11.2.1.3.3 Open the valve on the top of the ZHE to allow air in the headspace to escape. Cover the valve opening with a paper towel to reduce the chance of contamination as the piston sets. Gradually increase the flow of the nitrogen and monitor the pressure gauge on the ZHE. A distinct sound of the piston



setting should be heard as the pressure approaches 20 psi.

11.2.1.3.4 Once the piston is in position, close the valve on the top and remove the gas supply from the bottom of the ZHE. Open the pressure relief valve to release the nitrogen and close it immediately.

11.2.1.3.5 Determine the amount of extraction fluid to add to the ZHE by using the following equation:

$$\text{Volume (mL)} = \text{sample weight} \times 20$$

11.2.1.4 The sample is now ready to have the TCLP extraction fluid added. See Section 11.2 4.

11.2.2 Liquid TCLP sample preparation - If the sample is 100% liquid, then the liquid itself is defined as the TCLP extract. This liquid should be diluted and analyzed by SOP I-2-35.

11.2.3 Multiphasic TCLP sample preparation

11.2.3.1 Assemble the ZHE to the point where the sample can be added. See Section 11.2.1.1

11.2.3.2 Determine the percent solids of the sample as described in SOP I-1-15, Section 8.1.

11.2.3.3 If the sample contains less than 0.5% dry solids, the liquid portion of the sample, after filtration, is defined as the TCLP extract.

11.2.3.4 If the sample contains less than 5% but greater than 0.5% solids, weigh out a 500 g sample.

11.2.3.5 If the sample contains 5 or greater percent solids, then use the following equation to determine the weight of sample to charge to the ZHE:

$$\text{weight (g)} = \frac{25}{\text{percent solids}} \times 100$$

- 11.2.3.6 Transfer the sample the ZHE. If any sample remains in the weighing vessel, record that weight to determine the sample weight accurately.
- 11.2.3.7 Attach the top-plate to the ZHE as quickly as possible to minimize sample exposure to atmosphere.
- 11.2.3.8 Attach the gas supply to the bottom of the ZHE and open the valve on the top of the ZHE. Apply gentle pressure to force all headspace slowly out of the ZHE. When liquid appears at the top valve, close the valve and remove the gas supply.
- 11.2.3.9 Attach a pre-weighed Tedlar bag to the top of the ZHE. Apply pressure of 1-10 psi to force the liquid phase into the Tedlar bag. If no additional liquid has passed into the bag after 2 minutes, increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase, if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When liquid no longer flows at 50 psi, discontinue the pressure by closing the top valve and removing the gas supply. Reweigh the Tedlar bag to determine the liquid weight.
- 11.2.3.10 The material in the ZHE is defined as the solid phase of the sample and the filtrate is defined as the liquid phase. Save the liquid phase under limited headspace conditions for later analysis.
- 11.2.3.11 Some samples, such as oils or paints, will appear to contain material that is a liquid. Even after applying pressure this material may not filter. If this is the case, the material in the ZHE is defined as a solid and is extracted as such.
- 11.2.3.12 Determine the amount of extraction fluid to add to the ZHE using the following equation:

$$\text{Amount (g)} = \frac{20 \times \% \text{solids} \times \text{sample weight}}{100}$$

11.2.4 Addition of the extraction fluid - This section applies to all samples that

have solids to be extracted by the TCLP procedure.

- 11.2.4.1 The amount of TCLP Extraction Fluid 1 is determined in Section 11.2.1.3.5 and 11.2.3.12.
- 11.2.4.2 Use a 500 mL graduated cylinder to obtain the appropriate volume.
- 11.2.4.3 Using a syringe made of inert material and with Luer connection, transfer the extraction fluid to the ZHE through the valve on the top plate. Currently this lab uses a 30 mL teflon syringe which takes several fills of the syringe to complete the transfer. A 500 mL stainless steel syringe is available but has in the past damaged fittings on the ZHE's. This should only be used when no other syringes are available.
  - 11.2.4.3.1 Attach the full syringe to the valve on the top plate.
  - 11.2.4.3.2 Keeping pressure on the syringe plunger to avoid backflow, open the valve and force the liquid into the ZHE.
  - 11.2.4.3.3 Immediately close the valve and refill the syringe and repeat the procedure until all the fluid has been added to the ZHE.
  - 11.2.4.3.4 As fluid is added, pressure will increase that will make the addition of more fluid difficult. The pressure may be released at any time during the filling of the ZHE.
  - 11.2.4.3.5 The sample must be extracted with about 10 psi present. This can be achieved by carefully releasing the pressure when adding the fluid or by attaching the gas supply after the fluid has been added and then adjusting the psi to about 10.

#### 11.2.5 Rotation of the sample

- 11.2.5.1 Place the ZHE in the rotator. Record the initial psi and the time of the rotation start.
- 11.2.5.2 Rotate the sample for  $18 \pm 2$  hrs at  $30 \pm 2$  rpm.
- 11.2.5.3 Record the final psi and verify that the ZHE did not lose pressure during the rotation. If the pressure has not been maintained, the device is leaking. Check the ZHE for leaking and perform the extraction again with a new sample of waste. Also record the time the rotation was stopped and confirm that the time was adequate.

#### 11.2.6 Extrusion of the liquid from the ZHE's

- 11.2.6.1 Attach a Tedlar bag to the valve on the top plate of the ZHE. If the sample contained an initial liquid phase and this phase is miscible with the filtered liquid, then the same bag should be used and the liquids combined.
- 11.2.6.2 Connect the gas supply to the valve on the bottom plate of the ZHE.
- 11.2.6.3 Apply 10 psi pressure to the ZHE to force the liquid into the Tedlar bag. When liquid has ceased to flow for 2 minutes, increase the psi by 10 and repeat the procedure until 50 psi has been reached.
- 11.2.6.4 When 50 psi has been reached and no more liquid has been extruded for 2 minutes, close the valve on the top plate and remove the gas supply.

#### 11.2.7 Extract definitions

- 11.2.7.1 If the original sample contained no liquid phase, then the filtered liquid is called the TCLP extract.
- 11.2.7.2 If the original sample contained an initial liquid phase and this phase is miscible with the filtered liquid, they are to be combined and are collectively defined as the TCLP extract.
- 11.2.7.3 If the original sample contained an initial liquid phase and this phase is not miscible with the filtered liquid, the phase

volumes are determined, analyzed separately, and the results are combined using the following equation:

$$\text{Conc} = \frac{(V1)(C1) + (V2)(C2)}{V1 + V2}$$

where:

V1 = volume of the first phase (L)

C1 = concentration of the analyte in the first phase (mg/L)

V2 = volume of the second phase in (L)

C2 = concentration of the analyte in the second phase(mg/L)

11.2.8 Store the extract with minimum headspace until analysis. The hold time is 14 days for analysis. See SOP I-2-35 for analysis.

#### 11.2.9 ZHE cleanup

11.2.9.1 The ZHE's must be thoroughly cleaned after each extraction. The ZHE must be completely disassembled and all parts are to be washed with warm water and soap. Screens will usually require sonication in hot soapy water to remove particulates that have become trapped. All parts are to be solvent rinsed with methanol after being washed with the soap and water. Do not use acetone as this is an analyte and may cause sample contamination. The ZHE's are allowed to air dry. It is helpful to attach the base plate to the gas supply and turn on the gas to blow out any water from cleaning that may be trapped in the connections.

11.2.10 Analyze extracts by SOP I-2-35.

## 12.0 Data Analysis, Calculations, and Reporting Results

12.1 Results are reported in mg/L units and are determined by following SOP I-2-35.

12.2 If the sample contains 2 immiscible liquid phases, their analysis results are combined by the equation found in Section 11.2.7.3.

### **13.0 Method Performance**

Method performance is determined by evaluating sample results obtained after analysis and using the criteria detailed in SOP I-2-35 in Sections 9 and 13.

### **14.0 Pollution Prevention**

The solvents used in this extraction procedure are aqueous and pose no threat to the environment.

### **15.0 Waste Management**

There are no waste management issues associated with this method. Any excess samples or standards may be disposed of by rinsing down the drain with tap water.

### **16.0 References**

16.1 SW846 Method 1311, Toxicity Characteristic Leaching Procedure.

16.2 EPA Method 524.2, Measurement of Purgeable Organic Compounds in Water by Capillary Column Chromatography/Mass Spectrometry, Revision 4.1, Edited by J.W. Munch (1995).

### **17.0 Tables, Diagrams, and Flowcharts**

This section does not apply to this SOP.